Fully Relativistic Surface Green Function and Its Application to Surface Spectroscopies

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June 30, 1993

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Final LDRD Report

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Its Application to Surface Spectroscopies**

Tracking Code 93-IN-019

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MASTER

Fully Relativistic Surface Green Function and Its Application to Surface Spectroscopies

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A fully relativistic layer-KKR formalism was developed and implemented for calculating the single-particle Green function in atomic layers parallel to crystalline surfaces of magnetic and non magnetic materials: The method was applied to the calculation of surface spectroscopies, such as low energy electron diffraction (LEED), angle-resolved ultraviolet photo emission spectroscopy (UPS), and photoelectron scattering. Numerical tests were performed for non magnetic actinide surfaces and magnetic Fe surfaces. Theoretical angle-resolved UPS spectra are presented for uranium monolayers on Pt(111) and for f.c.c. u(111) surfaces. We find that island formation can take place if a peak in the UPS spectra appears just before the Fermi energy immediately as u is deposited on Pt, and we suggest an experimental procedure for testing this prediction. An intensity map of photo excited electrons from the $2p_{3/2}$ core states of Fe(110) surface is also shown. Sizable magnetic anisotropy is found due to the interference between exchange and spin-orbit interaction, which is suitable for studying a possible surface-induced magnetism of actinide adlayers.

Introduction:

There are at least two advantages in studying the chemical properties of materials by means of surface spectroscopies. First, one can easily control the geometrical arrangement of atoms on the surface by choosing suitable substrates and their chemical components. Especially the spacing between adatoms, which is mainly determined by the substrate-atom spacing, affects strongly their electronic properties such as magnetism and localization/de localization of electronic states. Second, one can apply directly well-established surface spectroscopic techniques, such as Low-Energy Electron Diffraction (LEED) to study desired properties.

The aim of this project has been to explore the electronic properties of monolayers on Pt and Pd substrates in collaboration with the ongoing experiment by Gouder and Colmenares [1]. In this report we study theoretically and computationally (i) angle-resolved Vacuum Ultraviolet Photoemission Spectra (UPS) from uranium monolayers on Pt(111), under the assumption that uranium can be grown epitaxially on the Pt(111) substrate, and (ii) photoelectron scattering spectra (PSS) from the $2p_{3/2}$ core states of the magnetic Fe(110) surface, and the onset of surface-induced magnetism of actinide adlayers due to rearrangement of unoccupied 5f electrons. In the first study, we also performed calculations for the f.c.c. u(111) surface regarding possible island-growth on the substrate. Since Pt and u are both elements with high atomic numbers, we have to definitely treat their scattering properties relativistically. In the study (ii), relativistic effects, particularly the spin-orbit interaction, play an important role. Here, we obtain magnetic information in terms of the magnetic anisotropy of the photoelectron-intensity-angular profile, which contributes to the interference between exchange and spin-orbit interaction. Our photo emission code is based on the fully relativistic spin-polarized layer Green function method, and yields layer-projected densities of states (DOS) of initial states which are helpful in analyzing photo emission spectra. Furthermore, we plan to apply the magnetic version of this code, which handles both magnetic and relativistic effects on the same footing, to the actinides or their compounds. This unique capability is particularly appropriate in this case, since the large nuclear charge in these systems entails strong spin-orbit coupling and the unfilled 5f-orbital electrons possess the potential of producing large magnetic moments.

Theory and Numerical Results:

A semi-infinite crystal model may be viewed as a stack of atomic layers extending infinitely in two dimensions parallel to the surface. The effective electron-solid interaction is approximated by muffin-tin (spherically symmetric) cell potentials which are obtained through an application of the LMTO (linearized muffin-tin orbital) method. The layer Green function is constructed in terms of the solutions of the Dirac equation taking into account scattering by other crystal atoms in the layer under consideration and by the adjacent layers.

In Figs.1 and 2 we show the angle- and orbital-angular-momentum-projected layer DOS for $\text{u/Pt}(111)$ and $\text{u}(111)$ in normal directions to the surface, which are obtained directly from the imaginary part of the Green functions. In this calculation, we assume an inverse lifetime of 0.2 eV so that we can regard the electronic states as holes of excited electrons (corresponding to Lorentzian broadening). Since f-electrons (thick solid line) are rather localized and, therefore, are relatively insensitive to the substrates, we find that the f-state DOS for a pure u surface is very similar energetically to that of a u monolayer on Pt (upper panels). It is true, however, that, f-electrons are more localized in $\text{u/Pt}(111)$ system than $\text{u}(111)$, simply because there is no way for f-state electrons to penetrate into the Pt substrate (lower panel in Fig.1). This can be seen very easily by switching off the lifetime broadening in the calculation. While the f-electron DOS approaches d-function-type features (u-layer induced surface states) in $\text{U/Pt}(111)$, it keeps the (narrow)-band features in $\text{u}(111)$.

In Fig.3, we show calculated spin-resolved UPS spectra for $\text{u/Pt}(111)$ and $\text{u}(111)$, for the case of an incident beam of light with positive helicity (circularly polarized). Spin-resolved spectra provide immediately an additional piece of information; the symmetry type of the initial states of photo excited electrons. For a (111)-surface normal, the crystal has C_{3v} (three-fold rotation and three mirror operations) symmetry and it is known that there are two types of symmetry groups, L_{4+5} and L_6 . In our spectra spin-up and spin-down intensities correspond to L_{4+5} and L_6 symmetry, respectively. Investigating the dipole matrix elements, a task which is not possible experimentally, we can trace back from the excited (final) states to the initial states and identify the physical origin of all spectra. In UPS spectra for $\text{u/Pt}(111)$ (upper panel), all peaks are of electrons excited from the Pt substrate (mainly from d-states), while only f-state electrons are exclusively excited from $\text{u}(111)$ surface (lower panel). These are rather surprising results, since the main contribution to UPS spectra usually originate from the topmost layer due to the short escape length of excited electrons (3 eV is assumed for excited states in terms of inverse lifetime) whose DOS's are similar for both $\text{u/Pt}(111)$ and $\text{u}(111)$. Checking the matrix elements closely, we find that final-state d-waves in $\text{u/Pt}(111)$ are very weakly excited in contrast to $\text{u}(111)$, where there are dominant dipole-allowed states in transitions from f-initial states. This type of complication has been found in UPS analysis, so that UPS spectra do not directly reflect the DOS of initial states. Furthermore, we predict that island formation takes place if a peak appears just below the Fermi level immediately as u is deposited on Pt substrate.

In Fig.4 we show the calculated intensity profile of photoelectrons from the $2p^{3/2}$ Fe core states of the Fe(110) surface excited by linear polarized light of energy 800 eV. The magnetic moment and the radiation field, E , of light are both parallel to (001) direction (y -direction) in the surface plane. Typical dipole-radiation intensity profile (top-heavy snowman form) is modified due to multiple scattering by the surrounding atoms. Since the magnetic moment lies on the y -plane, which is perpendicular to the surface including the y -axis, the y -plane is not a mirror plane any more and we find a left and right asymmetry pattern. This is exactly the magnetic anisotropy effect induced by the interference between exchange and spin-orbit interaction, which vanishes when either exchange or spin-orbit interaction is missing. In principle, this allows one to obtain information on the magnetic behavior of the Fe(110) surface by means of a comparison with experiment. Since sizable asymmetry is already found for materials with a small atomic number, such as Fe, we expect a larger effect in the actinides materials.

Summary:

We investigated theoretically and computationally UPS spectra from w /Pt(111) and u (111) surfaces and PSS spectra from Fe(110). In the former case, the results obtained are consistent with the experimental findings by Gouder and Colmenares [1], who performed experiments with polycrystalline Pt substrates. Further investigation seems necessary, using single-crystal substrates, in order to compare with the theoretical analysis. In the second study, we also suggest that PSS is a good candidate for studying the electronic and magnetic properties of actinide surfaces and suggest an experiment for the magnetic actinide-compounds surfaces such as US.

References:

- [1] T. Gouder and C. Colmenares, "LDRD project"

Publications:

- E. Tamura, "General theory of Low-Energy Electron Diffraction and Its Application to Surface Spectroscopies.(to be submitted Phys. Rev. B)"
E. Tamura, "Theoretical study on UPS spectra from w /Pt(111) surface (in preparation)

Presentations:

E. Tamura, "Surface as a New Stage for studying Actinides", Workshop "Synchrotron Radiation in Transactinium Research" in Lawrence Berkeley Laboratory, 1-2 Oct.,1992

E. Tamura, P.A. Sterne and A. Gonis, "X-Ray Absorption Dichroism in Magnetic Surfaces, APS March meeting in Seattle, 22 - 26 Mar. 1993"

Figure Captions:

Fig.1 Layer density of state of u/Pt(111) surface: u overlayer (upper panel), Pt bulk layer (lower panel). Total density of states is drawn with thin solid line, d-state with thick dashed line and f-states with thick solid line. The Fermi level is referred to zero.

Fig.2 Same as Fig.1, but for U(111) surface.

Fig.3 Spin-resolved UPS normal emission spectra from u/Pt(111) (upper panel) and u(111) surfaces (lower panel) by circularly polarized light of 21 eV: spin-up intensities (thick solid line), spin-down intensities (thick dashed line) and total intensities (thin solid line).

Fig.4 Spin-resolved photoelectron-intensity map from ferromagnetic Fe(110) surface. The magnetic moment lies in Fe(110) surface plane and is parallel to (001) direction (y-direction). The photoelectrons are excited into fixed kinetic energy of 92 eV from $2p_{3/2}$ core states by linearly polarized light with **E** parallel to y-direction.

Fig 1

Fig. 2

Fig. 3